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THE FORMATION OF CATION RADICAL FROM ANTHRACENE PEROXIDE DERIVATIVES IN LIQUID SULFUR DIOXIDE

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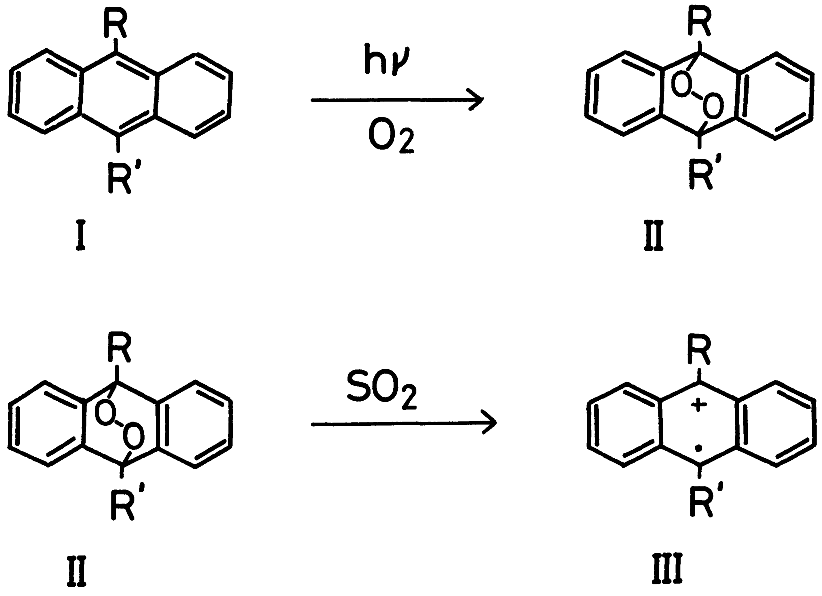
A novel formation of a cation radical from anthracene endoperoxide in liquid sulfur dioxide was reported. By the reaction of 9,10-epidioxy-9,10-dimethylanthracene, 9,10-epidioxy-9,10-diphenylanthracene, and 9,10-epidioxy-9-phenylanthracene in liquid sulfur dioxide, the corresponding cation radicals were formed immediately. With the use of catalytic amounts of these peroxides, the flash polymerization of styrene was accomplished in liquid sulfur dioxide.

It has been reported before that a cationic polymerization of styrene was found to take place in the presence of anthracene (Ia) in liquid sulfur dioxide-oxygen system.[1,2] It was presumed that a cation radical (IIIa) of anthracene was first formed, followed by the formation of styrene cation radical by electron transfer from styrene to IIIa. Tetraphenylethylene and diphenylethylene were found to form the corresponding cation radicals in the same reaction conditions,[2] and at that time it was suggested that the cation radicals were produced by the direct transfer of an electron of the hydrocarbon to the oxygen molecule in liquid sulfur dioxide.

During the course of the investigation on this interesting behavior, we noticed that the ionization potential of hydrocarbon has no relation with the formation of cation radical and the ability to polymerize styrene in this system. Only anthracene and phenyl-substituted alkenes can serve for these unique reactions.[2] These hydrocarbons are well known to react with singlet oxygen forming cyclic endoperoxides (II) as the stable compound or an intermediate.[3]

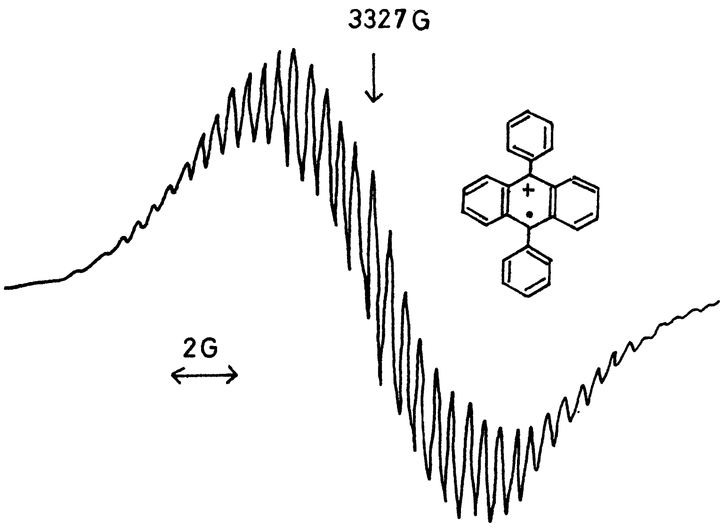
In order to check the possibility that the endoperoxide (II) of an aromatic hydrocarbon (I) works as the precursor of the cation radical, reaction of 9,10-epidioxy-9,10-diphenylanthracene (IIe) was undertaken in liquid sulfur dioxide in the absence of oxygen. When IIe (10 mg, 2.8 x 10^{-3}mmol) was dissolved in 5.5 ml of liquid sulfur dioxide, 9,10-diphenylanthracene cation radical (IIIe) was found to form immediately by the measurement of uv spectrum, λ_{max} ; 717, 650, 590 and 550 nm. The maximum yield of IIIe, which was measured by the absorption of λ_{max} 717 nm, was 20 %. From the reaction mixture 9,10-diphenylanthracene (Ie) was isolated in 40 % yield after two day reaction. Esr spectrum of IIIe was also observed having 41 splittings and $a_H(o)=a_H(p)=0.42$ G which was identical with that obtained by the reaction of IIe with sulfuric acid in n-hexane by Weeler, Sauthanam, and Bird.4) From 9,10-epidioxy-9,10-dimethylanthracene (IIc) and 9,10-epidioxy-9-phenylanthracene (IId), the corresponding cation radicals (III) were also obtained in the same reaction conditions.5)



a: $R=R'=H$, b: $R=CH_3$, $R'=H$, c: $R=R'=CH_3$, d: $R=C_6H_5$, $R'=H$, e: $R=R'=C_6H_5$

The polymerization of styrene was observed by the reaction with catalytic amounts of IIa, IIb, and IIc, respectively, in liquid sulfur dioxide in the absence of oxygen.6) When, for example, the mixture of 2.1 x 10^{-2} mmol of IIc and 8.0 mmol of styrene in 5.0 ml of sulfur dioxide was kept at 0°C for 10 min in the glass pressure bottle, polystyrene was obtained quantitatively with no contamination of polysulfone.7)

Considering these results, we reexamined the polymerization of styrene in the aromatic hydrocarbon-oxygen-sulfur dioxide system and found the necessity of light for this reaction. In the dark styrene did not polymerize at all and the polymerization was clearly accelerated by the irradiation of light. When the solution of 5.6 mmol of styrene, 1.3 x 10^{-1} mmol of Ia, and 15 ml of oxygen in 4.0 ml of sulfur dioxide was irradiated with a 300-w incandescent lamp from distance of 20 cm at 0°C for 1 hr, 88 % yield of polystyrene was obtained.2)



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2) T. Nagai, T. Miyazaki, Y. Sonoyama, and N. Tokura, J. Polym. Sci., Part A-1, 6, 3087 (1968).

3) L. O. Weeler, K. S. V. Santhanam, and A. J. Bird, J. Phys. Chem., 70, 404 (1966).

4) R. W. Denny and A. Nickon, "Organic Reactions," Vol. 20, ed. by W. G. Dauben, John Wiley & Sons, New York, N. Y. (1973), p. 133.

5) In the case of 9,10-epidioxy-9-methylanthracene, (IIb), the formation of 9-methylanthracene cation radical (IIIb) was not detected by esr spectroscopy, but 9-methylanthracene (Ib) was obtained in 25 % yield after 2 days reaction.

By dissolving 9,10-epidioxyanthracene (IIa) in liquid sulfur dioxide, the esr spectrum consisted of 3 broad lines with the coupling constant of 2.7 gauss was observed.

6) When IId was used as the catalyst, only 6 % of polystyrene was obtained by the reaction for 4 hr. In the case of IIe, polymerization did not occur at all in the reaction conditions probably due to the stability of cation radical IIIe.

7) Under the presence of α,α'-azobis (isobutyronitrile), the copolymerization of styrene and sulfur dioxide occurs. W. G. Barb, J. Polym. Sci., 10, 49 (1953).

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